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Significant progress has been made in the last several years toward the production of a highly conductive carbon filament. Graphitized carbon fibers, made from a variety of precursor materials such as PAN, pitch and benzene have electrical conductivity in the range 10^{-6} - 10^{-7} Ω m, tensile strength in the range 1/3 GPa, tensile modulus in the range 100-700 GPa and density in the range $1.8-2.2\times10^3$ kg/m³. These properties suggest

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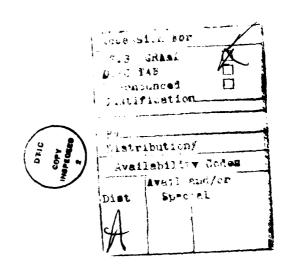
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20. ABSTRACT (Continued)

graphitized fibers may have potential as current carrying material for electrical power transmission. This paper reviews the physical reasons for the electrical and mechanical properties and evaluate prospects for better conductivity without degradation of mechanical properties. Chemical doping (intercalation) is found capable of achieving X5-15 improvements in conductivity with some degradation in tensile strength. Various applications for electrical power transmission usage are examined, i.e., underground and overhead conduction, underground pipe, overhead towers and submarine cable. Near term usage is most probable in towers and submarine cable where high strength to weight advantages may offset the good, but not great, fiber electrical conductivity.

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AN ASSESSMENT OF GRAPHITIZED CARBON FIBER USE FOR ELECTRICAL POWER TRANSMISSION

I. INTRODUCTION

Graphite is an anisotropic lamellar solid with physical properties which compare favorably with those materials used conventionally in electrical power transmission. In Table 1, one can compare the mechanical, thermal and electrical characteristics of the graphite a-axis to the properties of copper, aluminum, the 6201 aluminum alloy used for all aluminum power transmission lines, and a zinc coated stainless steel used for mechanical support with the weaker metals. (1) The properties of the graphite a-axis are equivalent or better in all respects except for a deficiency of a factor of 10-20 in electrical conductivity. However, there are known ways to chemically modify the graphite by intercalation which improve the conductivity by factors of 10-20. (2,3,4) Figure 1 shows examples of that improvement for several chemical species; note that the improvement is substantial (~X10) over a wide range of intercalant concentrations. The mechanical and electrical properties of graphite are impressive and, if one normalizes to unit weight, the low density of carbon accentuates those properties compared to other materials (see Figure 2).

While the a-axis properties of graphite are impressive, they are not very useful for power transmission unless carbon can be shaped to impart those properties along the axis of a filament. In fact, carbon chemists have been quite successful in incorporating the desired a-axis graphitic properties into the axial properties of a fiber (Table 2). Carbon fibers with high strength to weight ratios are presently exploited in graphitized carbon fiber/epoxide composites. These composites have had much publicized use in golf club shafts and tennis rackets. They will find increasing use as replacements to conventional structural materials in aircraft, automobiles and other areas where strength to weight ratios are a growing Manuscript approved November 1, 1982.

TABLE 1

PROPERTIES OF CONDUCTIVE MATERIALS USED IN POWER TRANSMISSION

	C10500 Cu	1350-II19 A1	6201-T81 A1 A110y	AISI-SAE 1078 Zinc Coated Steel	Single Crystal Graphite (a-aris)
Density in 10 ³ kg/m ³	ø.	2.7	2.7	7.8	2.26
Electrical Volume Resistivity at 20°C in 10 ohn -n	1.7	.8	3.2	19	40
Temperature coeff. of Resistance per °C at 20° C	.004	.004	.003	.004	.002
Thermal_Conductivity in 10 watts/m °K	e.	2.3	2.0	0.5	m
Coefficient of Linear Expansion per °C x 10	11	23	23	n	-1.5
Tensile Strength GPa	0.3	.2	0.3	Ħ	20
Young's Modulus GPa	120	70		200	1000

Metal properties from Ref. 1

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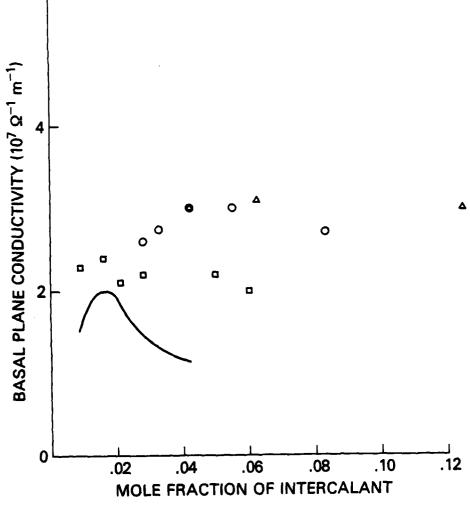


Figure 1. Basal plane electrical conductivity of graphite with various intercalants: O C_{6n} HNO₃ (Ref. 4), \triangle C_{8n} AsF₅ (Ref. 4); \square C_x Br₂ (A.R. Ubbelohde, Proc. Roy Soc London A327, 289 (1972)), — various alkali graphite intercalation compounds (E. McRae, D. D. Billand, J.F. Mareche and A. Herold, Physica 99B, 489 (1980)).

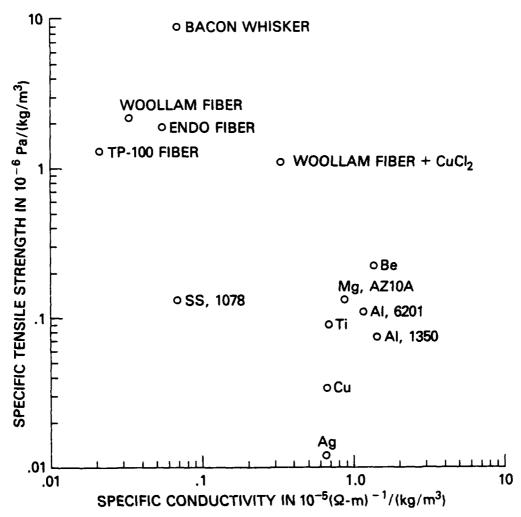


Figure 2. The specific tensile strength, i.e. normalized to unit density versus the specific conductivity for various materials. The metal alloys have their ASM identification. The other materials are carbon and can be found as follows: Woollam, Ref. 37; Endo, Ref. 12; TP-100, Union Carbide Sales literature; Bacon, Ref. 10.

TABLE 2
SAMPLE PROPERTIES OF GRAPHITIZED CARBON FIBERS¹

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		STATES OF GRAFILLIZED CARBON FIBERS	JO COLL	OKAFILL	77 mays	KEON FIL	SERS			
Nanufacturer Precursor	Celanese PAN	lane se PAN	Hercu	Hercules PAN	d	Union	Union Carbide	de Pitch	Benzene	Graphite
•	<u>6Y-70</u>	<u>GY-50</u>	V S	HMS	T-50	T-300	P-100	P-55		B-BX1S
Density kg/m ³	1.9	1.8	1.8	1.8	1.8	1.7	2.1	2.0		2.26
Electrical volume Resistivity at 20°C in 10 ohm-m	9	1000	4700	1200	950	1800	250	750	80	4
Thermal_Conductivity in 10 watts/m °K			.26	1.2	0.7	.85		1.0		m
Coefficient of Linear Expansion per °C x 10			-0.4	-0.5	-0.7	-0.5		6.0-		-1.5
Tensile Strongth GPa	1.8	2.4	3.1	2.2	2.4	3.1	2.4	2.1	4.	20
Young's Modulus GPa	520	350	230	370	390	230	700	380	180	1000

10-8 kg/m = 0.036 lb/in³
10 ohm-m = 1 μohm-cm = 6 μohm-cir mil/ft
1 GPa = 0.145 Mpsi
10 W/m oK = 58 Btu-ft/hr-ft²-eF

Commercial fiber properties from company technical literature, benzene decomposition fiber properties from Ref. 12.

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concern. The fibers in these high strength composites have moderately good electrical conductivity $\sigma \sim 10^5$ $(\Omega m)^{-1}$ and excellent tensile strengths (~3 GPa). From the perspective of power transmission the critical question is whether the conductivity can be raised to $\sigma \sim 10^7 (\Omega m)^{-1}$ while retaining the mechanical strength.

There are problems to surmount before one might develop and utilize the properties of graphitized carbon fibers for power transmission. How much more of the a-axis properties of graphite can be imparted to the filament configuration? Will the chemical modification schemes necessary to improve the electrical conduction in pure graphite also work in the fibers? Will the modifications be stable for years or tens of years? Will modification impair the other desirable properties? Can appropriate graphite filaments, which now cost on the order of \$1000/1b., be made cheaply enough to compete with conventional materials? The following report will examine these questions and assess the technological and economic problems facing the use of carbon fibers for electrical power transmission. One can anticipate the general answer. In the near term, graphitized fibers will likely be useful only in those selected applications chosen so that the unique properties of the fibers will permit new design possibilities which offset the fiber cost.

In Section II the fundamental chemistry and physics which impart to graphitized carbon its unique properties are examined. In Section III the possible application of fibers to power transmission are discussed in more detail. Several specific applications where the fiber properties have special potential are examined. Some conclusions and recommendations are presented in Section IV.

II. CARBON FIBER PROPERTIES

A. Manufacture

Most commercial graphitized carbon fibers are presently made from one of three precursor polymeric material: rayon, polyacrylonitrile (PAN) or pitch. The general processing procedures follow the sequence: the fiber is formed, stabilized, carbonized, and then graphitized. (5-11). The polymeric fibers are first stabilized via an oxidation process to increase the char yield and/or retain any axial alignment imparted during fiber formation. The stabilized polymer is then pyrolyzed in the vicinity of 1000°C. This removes most of the foreign atoms (0, N, etc.) and begins the growth of extended hexagonal networks. To some extent the carbon can now be viewed as sheets of two dimensional polymer made from phenyl rings. Further heat treatment at higher temperature extends the networks and leads to the formation of three dimensional islands. The islands have a turbostratic graphite structure, i.e., the two dimensional planes are stacked, but are rotationally misoriented. Higher temperature treatments (2000-3000°C), where the planes reorient to form the ABAB three dimensional graphite structure, are referred to as graphitization. Both carbonization and graphitization processes are likely to be done with the fibers under tension to orient networks parallel to the fiber axis. The carbon in a graphitized fiber is believed to be a set of tangled ribbons or sheets of layered networks (see Figure 3). The size of the networks, their preferred orientation, and the extent of layering depend on the starting material and the processing parameters. Structural alignment is generally better with higher processing temperature and strain.

An alternative technique for producing high quality graphitized carbon fibers has been developed by Endo and coworkers. (12) They form the

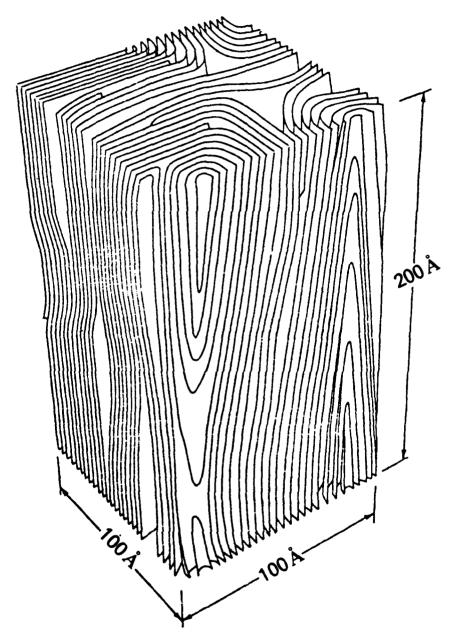


Figure 3. Schematic representations of the interpenetrating ribbons and planes of carbon which are believed to reflect carbon fiber structure (after B.J. Wicks, J. Nucl. Mater. <u>56</u>, 287 (1975)).

fiber by pyrolyzing a mixture of benzene and hydrogen at temperatures around 1100°C. The fibers are subsequently graphitized at temperatures above 2800°C. Fibers made in this way, and those made from mesophase pitch (13) by conventional spinning techniques, show the greatest potential for very high electrical conductivity.

In carbon fiber manufacturing technology the structure of the polymer precursor, the nature of the precursor treatment, and hot stretching all play a significant role in final fiber properties. But, in general, the desired properties in all carbon fibers improve with higher heat treatment temperatures (ETT). One can study the increased ordering caused by heat treatment and strain by means of X-ray diffraction techniques. (10,14,15,16, 17,18,19) The averaged planar spacing can be measured from the 00 ℓ diffraction angle. The polar width of the 00% lines provides an estimate of the coherence length L_c (i.e. number of stacked planes $n = L_c/d$) (10,14,20); the azimuthal width ϕ of the 00 ℓ lines provides an estimate of the preferred orientation of the crystallites. (10,15,19,21) One can also measure a coherence length L for the in-plane hexagonal network from the widths of the (hkO) diffraction lines. (10,14,15,22) Given the structure shown in Figure 3, the measured coherence length is likely to be related to a radius of curvature rather than the true extent of the hexagonal network. The evolution of order with heat treatment temperature (HTT) and strain is illustrated in Figures 4 and 5.

Microstructural observations of fibers by optical, high resolution scanning electron microscopy and scanning transmission electron microscopy have also contributed to the knowledge of fiber structure. (16,17,23) Three basic microstructural types are commonly recognized in graphitized carbon fibers: radial structures with a preshaped missing wedge, random structures,

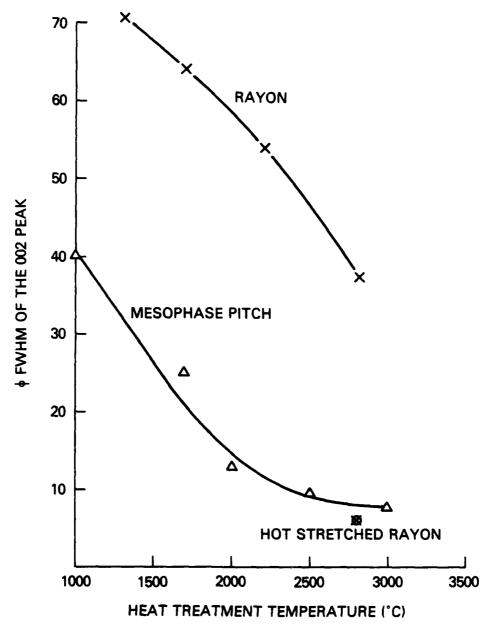


Figure 4. Preferred orientation of carbon layers parallel to fiber axis as reflected in the full width half maximum angular spread of the 002 peak in X-ray diffraction. The rayon data from Ruland, Ref. 51; the mesophase pitch from Bright and Singer, Ref. 50.

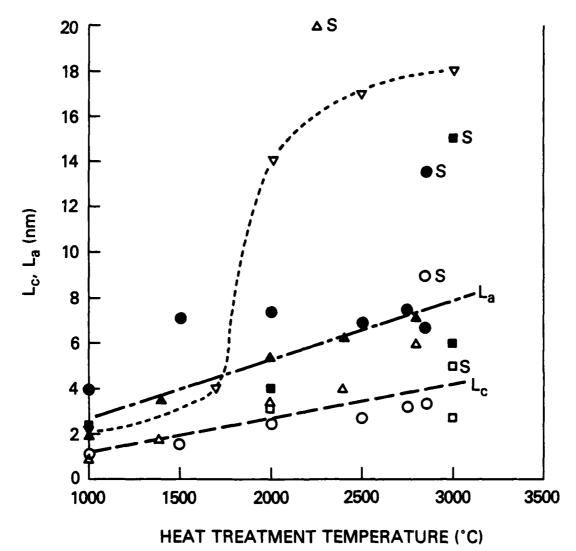


Figure 5. The coherence lengths L_c and L_a as measured by X-ray diffraction line profiles for carbon fibers subjected to various heat treatments; the letter s designates heat treatment with applied stress. L_c corresponds to the length along the c-axis; L_a along the a-axis. The data comes from: o, pitch fibers from Hawthorne, Ref. 16; A, PAN fibers from Johnson, Ref. 17; pitch fibers from Johnson, Ref. 22; F, mesophase pitch fibers from Bright, Ref. 50.

and onion skin. Scanning electron microscopy of GY-70 and TP 4104B, two highly graphitized fibers which are mentioned extensively in this report, showed concentric and radial structures, respectively. (24)

One interesting result of NRL research has been the discovery that nuclear magnetic resonance of fluorine-bearing intercalants in the fibers can be used to study the fiber microstructures. NMR has been shown to confirm the X-ray diffraction conclusion that orientation of the graphitic c-axis is perpendicular to the TP 4104B fiber axis. (25)

The general trend toward improved graphitization with ETT as demonstrated by L_a, L_c and ϕ in Figures 5 and 4 are consistent with changes in electrical conductivity (Figure 6), in elastic modulus (Figure 7 left), and in tensile strength (Figure 7 right). The preferred orientation of c-axis perpendicular fiber axis is precisely what is needed to maximize the fiber electrical conductivity and tensile modulus. As a general rule, soft carbons (such as from a mesophase pitch precursor) provide better electrical and mechanical properties than do hard carbons (such as from a PAN precursor) for a given treatment temperature. Soft carbons are also characterized by being relatively more soft mechanically and by graphitizing more readily at lower temperatures.

Because the HTT is not sufficient in itself to specify fiber properties, it is important to have some way in which to correlate their properties. The ordering parameters L_a , L_c and φ are not commonly cited in the literature. The value of the conductivity itself is frequently measured and is likely to be a good indicator of fiber potential. The work of Ezekiel (26) and others (10,27,28) has shown that the values of the tensile modulus and electrical conductivity are closely related.

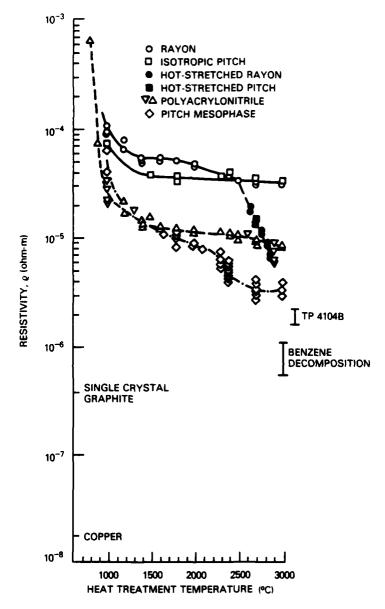


Figure 6. Resistivity as a function of heat treatment temperature HTT for various carbon fiber types. (Data points from D.B. Fischbach and K. Komaki, Extended Abstract, 14th Biennial Conference on Carbon, American Carbon Society (1979), page 191; Benzene data from Ref. 12).

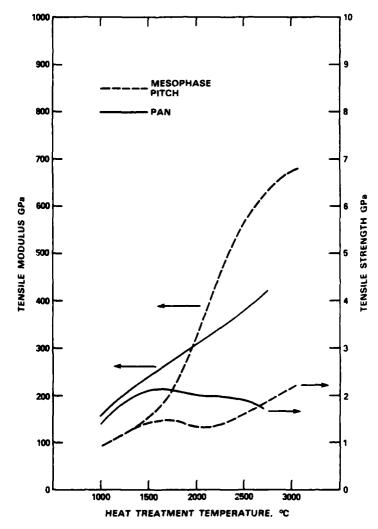


Figure 7. Carbon fiber tensile strength (right) and Young's modulus (left) as a function of heat treatment temperature. (Pitch data from Bright, Ref. 50, PAN data from Reynolds, Ref. 28).

B. Intercalated Fiber Electrical Conductivity: Empirical Development

The effect of chemical dopants on transport phenomena in carbons has been examined largely in a rigid band approximation. More extensive band calculations on intercalated graphite have been carried out to examine the modified electron density of states and the carrier effective mass, but little has been done on the less ordered systems such as fibers. However, there has been considerable research in recent years to determine empirically the effect of chemical dopants on fiber electrical conductivity. (24,29,30-37) The major results are summarized in Table 3.

One can draw several conclusions from the data in Table 3. First, the conductivity of carbon fibers can be improved by the same intercalants as in graphite. That improvement can be X10-25 for in situ measurements on highly graphitized fibers and X2-10 for residue compounds. When several fibers have been intercalated under the same conditions, the more graphitic fibers (as determined by σ (300°K) and E) improve the most. This observation is shown by the work of Herinckx (31) on rayon-based fibers with K as intercalant, of Goldberg and Kalnin (34) on PAN-based fibers with various fluorinated acceptors, and of the present work reported on PAN- and mesophase pitch-based fibers with K, Br, and IC1 as intercalants. Second, the relative improvement in fiber conductivity by a given intercalant can be greater than that observed for the same intercalant in graphite. Third, the intercalated fiber conductivity can be as high as $10^7 (\Omega m)^{-1}$. This is equivalent conductivity to iron $(\sigma = 10^7 (\Omega m)^{-1})$ and within a factor of 6 of copper ($\sigma = 5.8 \times 10^7 \ (\Omega m)^{-1}$). Fourth, the enhancement of fiber conductivity is always accompanied by the change of the temperature coefficient of resistance toward a more positive value. All virgin fibers showed negative TCR. The more graphitized intercalated fibers showed positive values of

TABLE 3. RESISTIVITY OF INTERCALATED CARBON FIBERS

		Fiber		E GPa	p(300°K)	TCR •K-1	Interc.	p _I (300°K) 10-° Ω-m)	TCR _I
	1. (31)	i	Rayon	200	930	-0.6x10-3	K (1)	20	+0.8x10-3
		WYD b. Union Carbide	Rayon		2300	-0.4x10-	K (1)	180	+.05x10-3
		WYB c. Union Carbide VYB	Rayon		0069	-0.9x10-3	K (1)	2500	-0.3x10-
	2. (32)	Union Carbide T-75	Rayon	200	089		HNO, (27)	80	
	3. (33)	a. Celanese GY-70	PAN	520	480	-1.5x10-s	HNO, (R)	100	-0.1x10-
		٠. ،					AsF, (R)	240	-1x10-3
16	4. (30,35)	35) Endo b. ''	Benzene		80	-0.1x10-	HNO, (27) HNO, (R)	12	+1.4x10-3
		 					Br ₂ (27) Br ₂ (R) AsF ₅	13 20 5	+0.9x10-
	5. (34)	a. Celanese b.	PAN	580	260		HSO, F SbF,		
				730	310		HSO, F+SbF, HSO, F SbF,	25 25 25 25 25 25 25 25 25 25 25 25 25 2	
		8. b.					AsF, HSO,F+Sb		
	6. (37)	6. (37) Union Carbide	Mesophase Pitch	650	150		CuC1,	10	

TABLE 3 (Cont'd)

TCR		4.4x10-3		+0.6x10-3						•	₹		+0.2x10-3	
ρ (300°K) 10-° Ω-m	20	70	12	40	30	320	770	100	001	710	70	0 ;	275	230
Interc.	Br ₂ (2?)	Br ₂ (R)	IC1 (11)	IC1 (R)	K(17)	IC1(R)	W(19)	TC1-B.	101 101	(a) -a-101	IC1 - Dr 2 (K)	101(11)	ICI (K)	V(17)
TCR • K-1	-2x10-3					-0.5x10-3		-1.5x10-3	1					
p(300°K) 10-* Ω-m	200					009		200						
E GPa	100							520						
	Hesophase Pitch				;	Mesophase Pitch		PAN						
Fiber	Union Carbide TP 4104B	• •	:	;		Union Carbide Mes. TP VSO-022 Pi	:	Celanese	GX-70	:	:	:	:	
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* Cross sectional area of intercalated fiber assumed to be twice original area.

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TCR, indicative of metallic-like behavior. Fifth, the conductivity enhancement can be stable in an ambient of air and at elevated temperatures. The work of Oshima et al. (37) on a mesophase pitch fiber (#6, Table 3) demonstrated air stability to 100°C. The residue compounds of Br₂ and HNO₃ were also air stable; the Br₂ residue compounds showed stable conductivity up to 300°C. Deitz and Hooley (38) have reported Br₂ residue compounds of TP 4104B can be stable up to 900°C in helium. Sixth, this work and that of Deitz and Hooley have shown that the more graphitized fibers intercalate more readily. For instance, TP 4104B intercalates Br₂ at (p/p₀)Br₂~0.6. For GY-70 Br₂ did not intercalate for (p/p₀)Br₂~1 and it was necessary to first intercalate IC1 which is known to intercalate more readily from work on graphite. The IC1 could be largely pumped away and Br₂ then inserted into the GY-70.

These experimental results demonstrate a potential for highly conductive, stable carbon fibers. But the research is not adequate to answer the question of how good one might make fiber conductivity. To answer that question one needs to know more about the basic physical/chemical processes which determine electronic transport in carbon and carbon fibers.

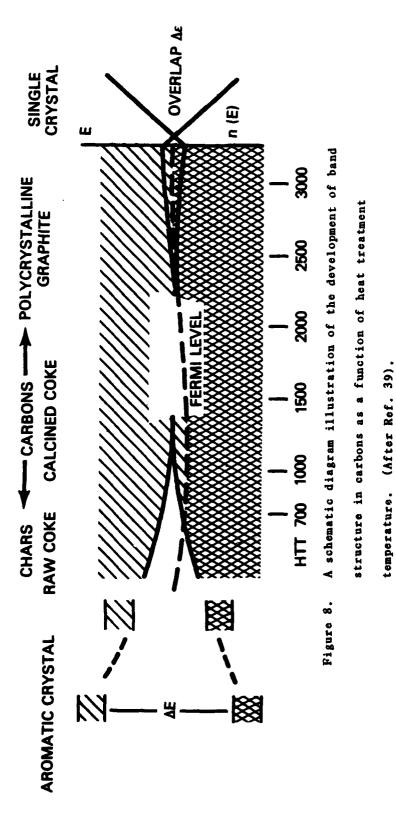
C. <u>Electronic Transport in Two Dimensional Conjugated Carbon Bonds</u>

The improvement of electrical conductivity of graphitized carbon fibers as the structure becomes more nearly like graphite suggests two things: 1) the mechanisms of a-axis conductivity of graphite can serve as a model for conduction in the fiber; the fiber will differ in the lack of three dimensional order and in increased defect sites; and, 2) the chemical dopants which enhance electrical conduction in graphite will also work in the fibers. The published work on carbon fibers confirms both hypotheses.

The properties associated with electronic transport in carbon fibers are not unique to that geometry. Various pyrocarbons, chars and cokes have also been examined as a function of heat treatment temperature. Conductivity, Hall coefficient, thermoelectric power, and magnetoresistance measurements and their temperature dependences have all been studied. A general review of this information has recently been published by Spain. (3)

In 1971 Mrozowski proposed a heuristic model for the carbon density of states to explain carbon electrical properties as a function of heat treatment temperature. (39) The model is schematically illustrated in Figure 8. The carbon $2p_{\pi}$ electrons in benzene form bonding/antibonding orbitals separated by 3.6 eV. As the two dimensional hexagonal network grows, these orbitals begin to form into the top and bottom of the valence and conduction bands, respectively. In a perfect network the valence band would be full, the conduction band empty and the Fermi level at midgap. However, the edge sites and other localized defects trap electrons. This extracts the electrons from the delocalized band structure and causes the Fermi level to dip into the valence band. At this point the carbon is a hole semimetal but the mobility is substantially lower than in graphite due to scattering by the numerous defect/boundary sites. As the planes grow in extent, and assume three dimensional ordering, the two bands migrate toward each other until they overlap slightly (40 meV). The number of defects decreases and the Fermi level migrates into the overlap region. This model has evolved somewhat in the past ten years but remains substantially intact. Bright has tested its present form against fiber transport measurements and achieved good agreement with reasonable physical values of five fitting parameters. (40)

It is likely that this picture, which presumes a free electron like behavior in the $p\pi$ bands, is not totally correct. Localized states at



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the band edges due to the presence of disorder in the two dimensional network are predicted by band theories. Localized states would lead to conduction by hopping mechanisms; there is evidence to support this mechanism in carbon and in carbon fibers. (3,29,41-43).

Band structure calculations on a two dimensional hexagonal network show that the valence and conduction band edges just touch at the Fermi level. (2,3) In crystalline graphite the interaction between planes, although weak, causes the two bands to overlap slightly (40 meV). The result is that graphite is a semimetal with a low concentration of holes and electrons (~10-4/C atom) but with very large mobilities (μ ~1 m²/V sec) because of small effective masses (m/mo~.06 - .004) and reasonable scattering times. The result is good electrical conductivity $\sigma = n_e \mu_e - n_h \mu_h = 2 \times 10^6 \ \Omega^{-1} \ m^{-1}$.

Chemical doping of the carbon-either by substitution of boron for carbon in the hexagonal ring, by intercalation, or by attachment to an edge site-provides an effective mechanism to change the number of available charge carriers. (44,45) The measurement of charge transfer in doped graphite has been inferred from a number of techniques. Most of the techniques are unable to directly probe the electron density local to the carbon nuclei. (2) Further, the techniques do not lend themselves to probing small heterogeneous materials such as carbon fibers. As one part of the NRL program we have explored the use of Auger spectroscopy to examine the density of states local to carbon in graphite and graphitized fibers. Auger is unique in that it not only directly examines the local density of states (as does X-ray emission spectroscopy) but it also can provide spatial resolution of less than a micron. That work (46) showed Auger to be sensitive to the charge transfer, but the quantitative extraction of charge

transfer was masked by screening. Work on the theory of screening in graphite is in progress so that ultimately the charge transfer can be extracted from the data.

Band structure calculations for some simple intercalated three dimensional graphites have been carried out in detail. (2) A rigid band approximation appears to work reasonably well for phenomenological work. Within a rigid band model for the density of states the chemical dopant simply contributes to (donor - Li, K, Cs, etc) or extracts from (acceptor - AsF_s , Br_s , HNO_s , etc) the conduction/valence band, respectively. This moves the Fermi level into a region of larger density of states (electrons for donor species, holes for acceptor) and electrical conductivity σ increases as the number of available carriers n increases. The charged dopant is also presumed to contribute an additional scattering mechanism, decreasing the net scattering time τ and thereby lowering the mobility μ :

 $\frac{1}{\mu} = \frac{m}{e} \left(\frac{1}{\tau} \right) \text{ phonon-elec} + \frac{1}{\tau} \text{ defect} + \frac{1}{\tau} \text{ dopant} \quad \frac{1}{\tau} \text{ elec-elec}$ Doping changes the carrier density more significantly than scattering time until large dopant concentrations are reached. This is thought to be the explanation for the peak in σ vs. intercalant molarity observed in Figure 1.(47)

The transport properties of a material are largely determined through the carrier concentrations n and mobilities μ . A number of studies of PAN, (26,48,49) mesophase pitch (50), and benzene decomposition fibers (30) have examined the temperature dependences of conductivity σ , magnetoresistance $\Delta \rho/\rho$ and/or thermoelectric power S in an attempt to determine the physical mechanisms dominating the transport. It is clear that defect and boundaries play a larger role in fiber than in crystalline graphite, but no study has definitively identified the physical mechanisms limiting fiber electron transport.

Mrozowski (39) recognized that doping of carbons could be a powerful tool for introducing large changes in carrier properties by small chemical perturbations. Endo et al. (30) have shown this for Br₂ residue compounds of their benzene decomposition fibers. We have demonstrated similar effects for Br₂ and ICl residue compounds in TP 4104B and GY-70 fibers (see Fig. 9). (A residue compound is used here to mean a sample intercalated under conditions leading to first or second stage intercalated graphite, the intercalant pressure is then removed by some prescription and the sample exposed to air.) Not only does doping improve the conductivity but it also changes the sign of the low temperature thermal coefficient of resistance. In both cases in Figure 9 maximum Br₂ or ICl residue is present. It may be possible to prepare samples with lesser Br₂ or ICl; this would be a significant tool in the investigation of fiber transport and in the role of dopants.

D. Fiber Mechanical Properties

As seen in Table 1, the tensile strength and Young's modulus for the a-plane of graphite are large compared to metals; Figure 2 demonstrates the even more impressive values when normalized by density. These properties are related to the very strong C-C bonds formed in the sp² hexagonal network. The fact that the electrical properties derive from the p_{π} electrons and the mechanical properties from the sp² electrons gives one hope that chemical schemes found to selectively alter the conductivity may not dramatically change the strength.

Carbon fiber strength and stiffness are expected to depend on the formation of extended two dimensional planes aligned parallel to the fiber axis. Studies of Young's modulus E in fibers confirm that expectation.

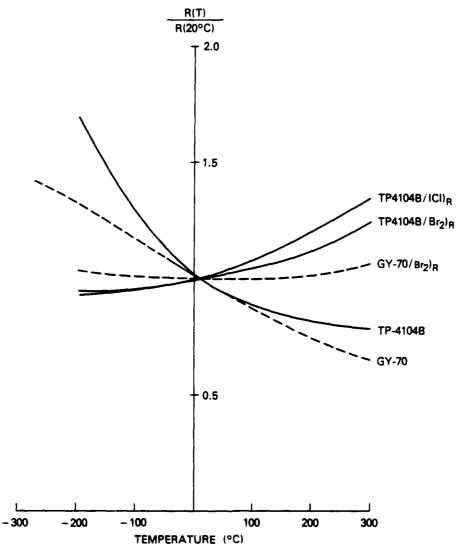


Figure 9. The relative change in resistance versus temperature for TP-4104B (a mesophase pitch precursor) and GY70 (a PAN precursor) fiber with and without intercalants. The residue compounds with Br₂ and IC1 (designated by subscript R) were prepared by fully intercalating the fiber and pumping off any volatile material. Note the change to a positive TCR in the residue compounds.

(10,16,19,28,50,51) It was shown earlier that the a-plane coherence length L_a (Figure 4), the c-axis orientation (Figure 5), and the tensile modulus and strength (Figure 7) all tend to improve with heat treatment temperature and applied stress. In Figure 10 the direct correlation of E with c-axis orientation is illustrated for a variety of carbon based fibers.

The peaking and slight decrease in tensile strength above HTT~1500°C in Figure 7 is thought to be due to increased sensitivity to flaws. (28) As the tensile modulus becomes larger, the fibers behave increasingly as brittle materials. Stress becomes concentrated about structural flaws which act as nucleation centers for crack initiation. Once a crack is initiated failure is catastrophic.

If the introduction of an intercalant or dopant into the carbon fibers results simply in charge transfer or bonding via the p_{π} electrons, then one would anticipate little change in the tensile modulus. However, swelling due to the physical insertion of the dopants may have some effect on modulus by modifying the alignment of the ''crystallite'' c-axes. This swelling might be expected to have a larger effect on the tensile strength than on the modulus of the fiber, since differential expansion between more graphitized and lesser graphitized regions should exacerbate flaws.

Changes in mechanical properties due to the treatment of fibers with chemicals known to augment conductivity in graphite cannot be unambiguously identified by reference to the literature. The chemistry is often complex, with chemical etching possible as well as intercalation. There are no comprehensive studies to isolate these two effects and each of the few available studies uses a different combination of fiber/chemical reagent.

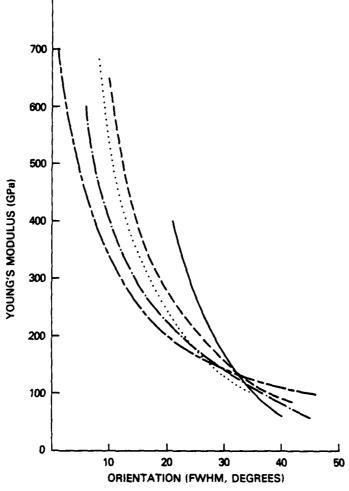


Figure 10. The Young's modulus E as a function of carbon layer orientation parallel to the fiber axis as measured by the full width half maximum angular spread of the 002 X-ray diffraction peak. The data are: _____, Fourdeax, Perret and Ruland, Ref. 19, this line represents the modulus (corrected for porosity) of rayon, PAN and pitch based fibers; _____ Hawthorne, Ref. 16, petroleum pitch, lignin coal and phenol formaldehyde based fibers;, Bright, Ref. 50, mesophase pitch based fibers; _____, Bacon Ref. 10, rayon based fibers; _____, Bacon, Ref. 10, PAN based fibers.

Hart and Pritchard (52) report considerable increases in modulus after oxidation of PAN fibers by NO, and air. They attribute the increase to etching away of the less graphitic materials. Kalnin (53) reports a study of a T-300 PAN fiber treated by strong intercalating acids (HNO₃/ H2SO2/H2O); depending on the acid composition he finds either little change or reduced tensile modulus and electrical conductivity. Again no evidence for intercalation was cited; the changes are attributed to internal oxidation of intercrystalline grain boundaries. Warner, et al. (54) report that PAN fibers (in particular, GY-70 and T-300) exposed to Br, and IC1 and then pumped to remove all but a small amount, show no change in tensile strength, modulus or electrical conductivity. However, they do observe increased plasticization in the presence of the Br₂. Goldberg and Kalnin (55) report similar plasticization of highly graphitized PAN when intercalated with AsF_s , SbF_s and HNO_s . Deitz (56) also reports work on six Br, doped and pumped PAN fibers; he finds ~50% increase in tensile modulus for the two most highly graphitized of six PAN fibers. None of the five studies cites any evidence to show the reagent actually intercalated.

Vogel (32) reports a study of a rayon based Union Carbide fiber T-75 (Table 3, #2); it was exposed to fuming HNO, under conditions known to intercalate graphite, but no diffraction evidence is shown for fiber intercalation. The conductivity increases by an order of magnitude, the modulus increases by 70%, and the tensile strength decreases by 20%. This contrasts with the study of Kalnin (53) who saw conductivity and strength decrease in his work with HNO₂/H₂SO₄/H₂O. The difference is likely to be in chemical etching which is accelerated by the presence of water. Kalnin suggests the etching may preferentially attack the 'amorphous' carbon and

''crystallite'' boundaries. Kwizera, et al. (24) report that the Young's modulus of GY-70 and TP 4104B fibers is not degraded as a result of intercalation by FeCl, AlCl, and alkali metals. Diffraction studies confirmed intercalation. Herinckx, et al. (31) report work on K intercalated rayon fibers which also shows little to no change in the Young's modulus. Tensile strengths are not reported in either work; Herinckx et al. attempted the measurement but failed due to bending at the point of fiber loading. Gillespie et al. (29) have reported that the tensile strength of lesser graphitized fibers (T-300, VS0022, AS, RMS) is lowered somewhat (10-50%) and highly graphitized fibers (TP 4104B, GY-70) substantially (~X10) by intercalation with K followed by exposure to FeCl.

Endo, Koyawa and Inagaki (30) have examined the modulus and tensile strength of fibers prepared by benzene decomposition and intercalated by Br, and HNO3. For air exposed fibers they found the tensile strength decreased by ~25% and 35% for Br, and HNO3 intercalation, respectively. The tensile modulus decreased by 10% at most. For HNO3~ exposed fibers, X-ray diffraction confirmed a high stage of intercalation. They also noted that the tensile strength varied inversely with fiber diameter.

With the exception of Kalnin's (53) work, the results of chemical treatment by reagents known to intercalate graphite show that Young's modulus is either unchanged or increases. The increase is attributed to improved alignment of crystallite c axis perpendicular to fiber axis.

The effect on tensile strength is likely to be detrimental but quantification is uncertain due to the difficulty of making the measurement.

For the use of graphitized carbon fibers in power transmission the tensile modulus E is an important property. On the basis of evidence to

date, heat treatment or chemical modification to enhance electrical conductivity is likely to improve, or at least not alter, the modulus. Tensile strength (TS) is another matter. Actually the problem with fiber application to power transmission lies not in the tensile strength itself. The strength of the highly graphitized intercalated fiber, while not as good as lesser graphitized carbon, compares very favorably with other structural materials (see Tables 1, 2 and Figure 2). The problem lies in the fragility of the fiber to bending; they are difficult to handle without breaking.

Since the presently known techniques to improve fiber conduction (HTT and chemical modification) have been shown to reduce the tensile strength, the fragility problem is serious. Several possibilities exist which might reduce the difficulties. First, fiber fragility is manifested in its inability to bend. One way to improve performance is to reduce the fiber diameter d. The radius of curvature R at which the fiber breaks is related to d by:

 $R = \frac{(d)E}{(TS)}$

Second, it has been observed by several groups, (11,28,30) that smaller diameter fibers have increased tensile strengths. This may be related to fiber structure. It is postulated that the outer shell of the fiber is more graphitized and carries most of the load. Smaller diameters may augment the proportions of graphitized carbon and may reduce the probability of flaws. Third, the susceptibility to failure of the highly graphitized fibers has been shown to be dependent on flaws. As ever shorter fiber segments are tested, the tensile strength has been shown to approach 1% of the tensile modulus, even for heat treatment temperatures at 3000°C. This observation demonstrates flaw sensitivity; the shorter the segment, the lower the

probability of a flaw. Manufacturing techniques and surface treatment have been developed to achieve the present state-of-the-art; they can be improved further to reduce the incidence of critical flaws.

Finally, one might imbed the fiber in a tough matrix material. Diefendorf (5) has pointed out that this process is not a panacea because the fiber modulus is so much greater than that of available polymers. However, it is possible that a high strength matrix composite will hold broken fibers sufficiently close to retain good conductivity. It is also possible that a composite utilizing electrically conductive polymers, such as polyacetylene which responds to the same dopants as the fibers, may be utilized to augment conduction between fibers.

III. Electrical Power Transmission and Distribution

A modern power system consists of a network of power stations interconnected by transmission lines generally rated at 115kV and above (see Figure 11). This network, also referred to as the Bulk Power System, is connected via the transmission lines to substations where the bulk power is divided into smaller units of power, usually at lower voltages. This power is directed toward load centers via a subtransmission and distribution system where the power is further divided at still lower voltages to points of utilization. In the United States and most developed nations, individual systems are also interconnected via transmission lines to provide reliability and economics of load diversification.

The vast majority of transmission lines are of the familiar overhead construction; in the United States approximately 99% of transmission mileage is overhead. However, this percentage does vary widely from region to region depending largely upon the degree of urbanization. The United Kingdom and New York State, as examples of land masses with similar urbanization, have 5-10% of the transmission lines installed underground. The reason for this picture is simple; underground transmission and distribution lines are substantially more expensive than overhead lines because of certain, thus far immutable (despite much research and development effort) technical handicaps borne by underground lines. These can be simply summarized as: 1) high material costs of electrically insulating underground cables as compared to the basically air insulation of overhead lines; 2) the vastly inferior thermal environment underground as compared to free air; this necessitates more conductor material to control I2R losses in underground applications; and, 3) higher installation costs,

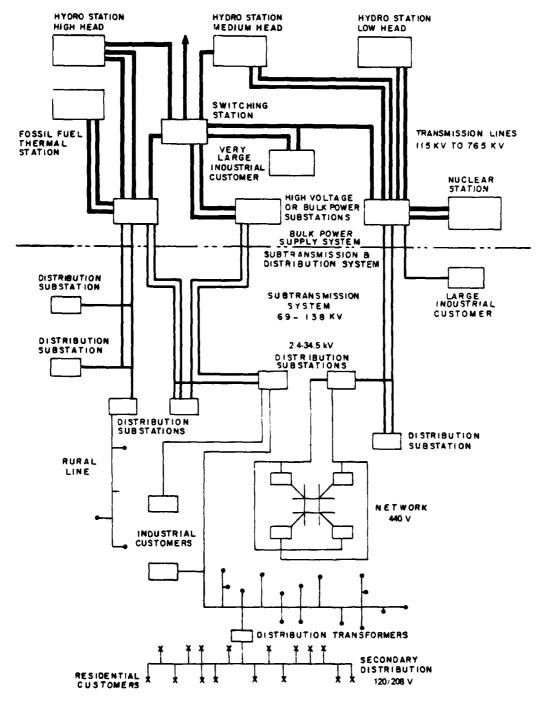


Figure 11. Outline of a Modern Power System (from Electric Utility System and Practices, text for General Electric course in Power Systems Engineering).

principally due to the high cost of excavation. A more comprehensive discussion of these factors can be found in references 57-60.

The conducting materials employed in state of the art transmission systems are primarily steel for overhead towers, guy wires, and pipes, and copper/aluminum for the actual electrical power conduction. A wide variety of alloys of each of these have been tailored to specific applications. One important family is the set of diamagnetic steel alloys for single phase riser pipes. Zinc and silver are used in modest quantities for various galvanizing and coating applications. In the following discussion we will the potential for graphitized carbon fibers to replace these metals in several of their major uses will be examined: cable conductor, overhead conductor, cable piping, overhead transmission towers, and submarine power cables.

A. Underground Cable Conductors

In low (0-600V) and medium (601V-35kV) voltage applications (distribution) both copper and aluminum conductors are used. The selection between them is based almost exclusively on prevailing economics with some favorable weighting given copper due to its relative ease of reliable joining and higher ultimate valve as scrap. Conductor weight and strength are only of peripheral interest as affecting shipping cost and unusually severe installation, respectively. These cables represent a high volume commodity with perhaps 20,000 to 30,000 miles of single conductor medium voltage cables installed annually in the United States. Much of this is in the so called underground residential distribution (URD) application where circuit loading is generally light; this permits use of the smallest Al conductors consistent with manufacturing and maximum dielectric stress considerations. The materials cost of a typical medium voltage, single conductor cable is \$3 to \$10 per foot depending on conductor size.

Conversely in high and extra high voltage cables, the utility faced with the high cost premium for underground transmission circuits generally aims to maximize cable rating by use of very large and almost exclusively copper conductors. Graphitized carbon fibers, with limits on their conductivity, are not a likely candidate for the high voltage underground cable conductor.

Since strength and weight are not important properties for the medium and low voltage cable conductor, the two main attractive features of carbon fibers are not assets. The fibers do have three lesser advantageous properties for this application. In cable design various techniques expanded conductors, segmented insulated spirally assembled conductors, enameled strands, etc. - are normally used to reduce the increase in AC resistance over the DC value. (AC/DC ratio ~1.2-1.4). The higher degree of graphitization in the outer layers of the fibers will mean that the skin effect which increases the AC/DC resistance ratio of a homogeneous conductor will be less deleterious. The anisotropy of the fiber resistivity, radial value likely higher than axial value, may also reduce the AC/DC resistance increase caused by proximity effects. The negative or small positive temperature coefficient of resistance (TCR) of the fiber will also reduce thermal dissipation problems. However, it is unlikely these advantages would be sufficient to offset the higher cost of the fiber, even if fiber stability and splicing were not problems.

B. Overhead Conductors

Overhead conductors, usually made from alloys and composites of aluminum/steel or aluminum/aluminum alloy, vary widely depending on both electrical and mechanical loading.

The conductors must conduct currents of 100's to 1000's of amperes in normal operation and 10's of thousands for brief periods (.15 sec.) during system faults. They must have sufficient strength to permit tension stringing in long spans to maintain minimum clearance to ground under all conditions of current loading and conductor expansion as well as wind and ice loading. They must survive occasional flashovers to ground without significant damage and must exhibit long-life under all conditions of exposure to the elements.

Finally, the conductor must be amenable to being configured to yield surface electrostatic stresses low enough (about 40 volts rms/mil) to control radio and audible noise to accepted levels. At the 345 kV and higher ratings bundled conductors - two, three and four conductor per phase - are frequently used to mitigate the corona which causes the audible and RF noise problems.

Two conductors per phase is common with a typical 345 kV rating and 1277 kCir mil size. The weight of a single conductor is 1.2 pounds per foot; its present cost is \$0.6 dollars per pound. Approximately 7000 miles of overhead line is added or replaced each year. Two conductors per phase, three phases per circuit and two circuits per tower gives an annual market of approximately 10⁵ miles of conductor.

In this application the graphitized carbon fiber strength to weight ratio becomes a definite advantage. An intercalated fiber with resistivity of $10\mu\Omega$ -cm would be within a factor of three of the resistivity

(long spans, ice loading)

~10x the tensile strength. For equivalent conductivity 3 times more volume (~2 times more weight) of carbon than 6201 alloy would be necessary.

However, the mechanical properties of the carbon would provide new tower and

insulator design possibilities, especially for unusual long span situations such as water crossings. It would not be necessary to use a steel cable between towers as is presently required to help support the aluminum conductor.

TABLE 5

Potential or Perceived Advantages/Problems

Carbon Fiber as Overhead Conductor

Advantages

Problems

High strength/weight ratio (long spans, ice loading)

Splicing

Low Temp. Coeff. of Expansion

Environmental Stability

Low Temp. Coeff. of Resistivity

Low skin effect

C. Pipe for Pipe Type Cables

Conventional underground conductors are usually housed in resistance seam welded carbon-steel manufactured to American Petroleum Institute (API) specifications with extra provisions covering weldability and interior smoothness. The pipes are flared to facilitate field butt-welding with an interior ''chill'' (backer) ring. Their interior is coated with an epoxy enamel which protects the surface from rusting in storage; their exterior is coated with mastic and/or extruded plastic coatings for long term corrosion prevention. The exterior coating degrades the pipe thermal transfer characteristics and contributes somewhat to the underground cable thermal problem.

Present applications at 138 kV-345 kV use either 8'' or 10'' pipe almost exclusively and in about equal quantities. The as-described current material costs are \$9 and \$12 per foot, respectively. Projected usage of the pipe type cables is about 50 miles/year through the '80's.

The pipe for high pressure pipe-type cables must withstand internal pressures up to about 500 psi in special cases - more usually 200 psi. The usual pressure medium is a mineral or polybutene oil; the temperatures up to about 70 degrees C. The pipe and its couplings or joints must be effective as a total vapor barrier against permeation of water, air and other vapors. It must be resistant to corrosion from all sources in a buried environment. The interior of the pipe must be smooth and abrasion resistant, and joints or couplings must not present any dimensional steps or irregularities so as to permit damage-free installation of delicate and heavy cables in long lengths. Changes in direction must be accommodated by field (preferred) or factory bends which must be of generous radii (50 - 300 ft. typically) and smoothly formed.

The pipe and couplings must be capable of repeatedly conducting fault currents up to typically 30,000 amperes for three to five cycles (.05 to .083 seconds) without physical or electrical degradation. Longitudinal resistance must be low enough to limit voltage build-up to safe levels, presently undetermined. The pipe need be nonmagnetic so as to reduce power losses.

TABLE 6

Potential or Perceived Advantages / Problems

Carbon Fiber Composite as Pipe

Advantages Problems Nonmagnetic (lower losses) Higher cost than steel pipe Rugged but lightweight Joinability Inherently corrosion resistant? Vapor resistance Available in tailored diameters Oil resistance Fault current limiting? Arc resistance

A carbon fiber/polymer composite pipe would offer several attractive features - strong, light, non-magnetic. The normal metal corrosion processes would not be a problem, but the oxidation and permeability characteristics of the polymer would need attention. The anisotropic resistivity characteristics of the fibers could be used to control the eddy and circulating current losses.

A second type of underground cable is gas (SF₆) insulated transmission line (GITL). Basically all the requirements enumerated above for pipe apply for the GITL with added emphasis on the need for corrosion resistance or protection for the aluminum alloys presently used in the pipe. GITL's are characterized by large diameters, this makes the outer enclosure a highly significant element of system cost. Because they are inherently high current systems, control of losses to tolerable levels is technically and economically demanding.

All commercial GITL's to date are of the three-single phase configuration. Designs with three phases in a common enclosure are being developed and demonstrated. Many of the points discussed here for the

single phase systems have validity for three phase by substituting ''eddy-current losses'' for ''circulating current losses.''

Sheath losses in laterally spaced configurations of single phase GITL's vary with sheath resistance and with spacing between cables. Higher spacings, desirable to mitigate mutual heating, result in higher induced sheath voltages. Where the sheaths are solidly bonded among phases, high circulating currents and I2R losses result.

In typical configurations of GTTL, sheath losses closely approach the conductor losses with accompanying heavy penalty in rating. For any given spacing and load current, the sheath losses vary with sheath resistance, peaking at some finite value. Accordingly, the designer strives to work off this peak. Clearly if the sheath resistance were zero, current would be infinite but losses would be zero (an impractical case); practically, where the sheath resistance is made to appear infinite by use of insulating sections or where the induced voltages are caused to phase cancel, current is zero and losses vanish. This is exploited in the various schemes of special sheath bonding; cross bonding, open circuited sheath operation, etc. Such schemes are employed in high power self-contained cable systems but pose problems of added equipment and higher maintenance costs. With the much larger diameter GITL's these problems appear to be significantly magnified (ideally the cables should be transposed frequently) and special bonding has not been practiced.

The combination in the graphitized fibers of high strength to weight ratio and ability to vary conductivity over a broad range appear to offer new degrees of freedom for design of these systems. Additionally, the presumed high corrosion resistance of a fiber/polymer composite is a very significant advantage relative to the corrosion prone aluminum sheaths employed presently.

D. Towers

Overhead transmission line towers usually employ (galvanized) steel as their structure either in the form of lattice (cross-braced) towers, fabricated from conventional structural shapes (angles, I-Beams, channels) or, importantly, as a compromise to environmental pressures, so-called ornamental designs, using rolled/welded tubular poles. Various forms of wood poles, laminates, H-frames, A-frames, etc., are employed chiefly with environmental urging rather than economics.

In addition to the support function, the conducting metal structure serves as a grounding path to dissipate atmospheric (lightning) and system (switching surge) induced overvoltages to earth. Wooden structures must, in order to serve the same function have a conducting ''down-lead'' usually of copper.

Strength and weight of these structures are important considerations relating to spacing of towers, foundation and erection costs and perhaps as importantly, placing of towers in areas of visual or environmental impact. Spacing of towers varies widely depending on route, topography, allowable height, weight of conductors, wind and ice loading, etc. but five towers per mile can be taken as representative for a 345 kV line, which we will use as a base line case. Towers are frequently designed to carry two circuits. Such a double circuit tower either in lattice steel construction or tubular poles typically weighs 25,000 pounds.

In 1980 there were in service approximately 285,000 circuit miles of overhead transmission lines at all voltages 115 kV and above with annual additions projected at about 7,000 miles per year. Thus, the annual market for steel towers can be projected at about 438,000 tons per year. At a fabricated steel price of \$750 per ton, the market is \$330 million/yr.

Overhead transmission lines have great exposure to atmospheric lightning induced overvoltages. Most important lines employ grounded conductors (steel or galvanized steel wires) disposed above the power conductors in such fashion to serve as shields for the transmission circuit. In the event of a lightning stroke near or to the line, inductance rather than resistance dominates the electrical response of such systems. A conductivity deficient, but strong, light-weight conductor might serve this function economically. Since inductance rather than fiber/composite resistance is likely to be the limiting factor in current flow, it should be possible to utilize a lesser graphitized carbon fiber, such as T-300 or As in Table 2 with a cost of ~ \$30/1b., instead of the more highly graphitized fibers. The carbon fibers presently manufactured have far better strength/weight characteristics than the 1078 steel used in power transmission. The response of graphitized carbon fiber composites to lightning strike has been evaluated by the aircraft industry; the composites were able to carry lightning current without damage but had some problems at joints.(61)

E. Armor Wires for Submarine Power Cables

Single conductor submarine cables offer compelling advantages over three conductor cables. Among these are the generally longer splice-free lengths which can be supplied and laid, and the ability to provide redudancy via a fourth single conductor cable rather than a second three-conductor cable.

As discussed above, single conductor cables have special problems of induced voltages and currents in their outer coverings. Steel wire has historically been the preferred armoring material for submarine cables because of its high mechanical strength, abrasion resistance, etc. Because

of high magnetic losses in single phase configurations, other non-magnetic materials have been employed (aluminum, copper) but with attendant reduction in mechanical protection - in certain cases disastrous.

The use of carbon fibers for the armoring could provide a high strength, non-magnetic alternative. Further, in the aqueous environment the weight advantage of carbon becomes even more pronounced. Buoyancy would leave the carbon with an effective density of one, while steel and other transition metals have an effective density of about 8. This difference in effective weight would be of special value where power cables rose off the sea floor, in Ocean Thermal Energy Conversion systems for example. The superior weight and mechanical characteristics of the carbon would far offset the inferior electrical characteristics.

IV. CONCLUSIONS

- 1. Graphitized carbon fibers, suitably modified by chemical dopants, can be made with $\rho < 10^{-3}~\Omega$ -m and stabilization under normal ambient conditions. It is likely that intercalated fibers with $\rho < 5 \text{x} 10^{-4}~\Omega$ -m will also be made since better fibers and dopant combinations will inevitably be found. Since the best intercalated graphite data show twice the resistivity of Cu, it is presently unrealistic to predict that intercalated fibers will have the resistivity of Cu.
- 2. Chemical doping of the carbon fibers increases their weight, but also increases their diameters. The two effects largely offset and leave the fiber density unchanged. The specific conductivity of doped fibers will thereby gain ~4X compared to Cu.
- 3. A negative temperature coefficient of resistance (TCR) is valuable for power transmission applications because local heating will not lead to increased power loss. The TCR for virgin graphitized fibers is uniformly negative, but less so the more highly conductive the fiber. This trend is continued for the chemically doped fibers, the better the resistivity the more positive the TCR. However, the room temperature TCR for the most conductive carbon fibers to date, TCR $\sim 1-1.5 \times 10^{-3}$ ($^{\circ}$ C⁻¹), are substantially lower than for Cu or A1, TCR $\sim 4 \times 10^{-3}$.
- 4. The fiber tensile strength in itself should be significantly better than Cu, Al or even steels. However, fragility of the highly graphitized virgin and chemically doped fibers are a significant problem. There are reasonable approaches to this problem which can be explored. Improvements are a certainty.
- 5. Fiber manufacturing technology is a problem because of the expense involved. The largest factor is the 3000°C heat treatment temperature

needed to achieve the higher degree of graphitization. The HTT requirements might be reduced by appropriate choice of precursor. It has been observed that graphitic ''preorder''and graphitizability increases in the order pitch, rayon, PAN, and mesophase pitch. The latter is a relatively new material and it is reasonable to expect improvements in its manufacturing technology. The benzene decomposition technology is also relatively unexplored. An alternative way to reduce energy requirements to reach the 3000°C temperature may be to heat the carbon fibers directly by passing electrical current through them or by RF inductive heating rather than conventional furnaces.

6. With the present level of research the transport mechanisms in carbon fibers are likely to be reasonably well understood in a few years.

The heretofore empirical studies of chemical doping as a means to change the conductivity will provide an important tool for developing that understanding.

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